

# Graphene-Based Ultra-Light Batteries for Aircraft

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NASA Aeronautics Research Institute

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### Outline

- The innovation
- Background
- Technical approach
- Impact of the innovation
- Results of the Seedling effort to date
- Distribution/Dissemination—getting the word out
- Next steps



### The Innovation

- Develop a graphene-based ultracapacitor prototype that is flexible, thin, lightweight, durable, low cost, and safe and that will demonstrate the feasibility for use in aircraft
- These graphene-based devices store charge on graphene sheets and take advantage of the large accessible surface area of graphene (2,600 m²/g) to increase the electrical energy that can be stored.
- The proposed devices should have the electrical storage capacity of thin-film-ion batteries but with much shorter charge/discharge cycle times as well as longer lives
- The proposed devices will be carbon-based and so will not have the same issues with flammability or toxicity as the standard lithium-based storage cells.



# Impact of the Innovation

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 Commercial ultracapacitors are currently being used in transportation. A fleet of buses near Shanghai has been running on ultracapacitors for the past several years.
 Only disadvantage: frequent stops due to low energy densities.



- Graphene-based ultracapacitors promise energy densities greater than existing commercial electrochemical ultracapacitors by an order of magnitude. They also have greater power densities than lithium-ion batteries by an order of magnitude.
- GO, the precursor for the production of graphene, is manufactured on the ton scale at low cost as opposed to lithium, which is a limited resource that must be mined throughout the world.
- A robust, lightweight, flexible, thin, and inexpensive energy storage device with energy and power densities superior to those of state-of-the-art energy storage devices will greatly benefit NASA and the nation's aeronautics.
- Such revolutionary energy storage devices will radically reduce the mass and weight of energy storage and supply devices resulting in more efficient aircraft.



# What is Graphene?

- Graphene is a revolutionary new allotrope of carbon (a single atomic layer of graphite)
   with extraordinary properties:
  - Surface area: 2630 m<sup>2</sup>/g
  - Electrical conductivity:  $10^6~\Omega^{-1}cm^{-1}$  (Cu:  $0.6x10^6~\Omega^{-1}cm^{-1}$ )  $\pi$ -electrons act like photons mobility is determined by graphene quality
  - Thermal conductivity: 5000 Wm<sup>-1</sup>K<sup>-1</sup> (Cu: 401 Wm<sup>-1</sup>K<sup>-1</sup>)
  - Strongest material ever discovered: Tensile strength ~ 130
     GPa (steel ~0.4 GPa)
  - "Graphene is complicated and expensive to make in large sheets" Nature, Nov. 20, 2013



# Background

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There are two main established methods for the storage and delivery of electrical energy:

- Batteries
  - Store energy with electrochemical reactions
  - High energy densities
  - Slow charge/discharge cycles
  - Used in applications requiring large amounts of energy → aircraft
- Electrochemical capacitors
  - Store energy in electrochemical double layers
  - Fast charge/discharge cycles
  - Low energy densities
  - Used in electronics devices Large capacitors are used in truck engine cranking





### **Current Aircraft Batteries**

- General Aviation and Light aircraft → Lead acid batteries
- Larger aircraft and helicopters 

  Nickel cadmium batteries
- Aircraft manufacturers are beginning to use Lithium Ion batteries due to their larger capacitances per unit weight.
  - Li-ion batteries still have low power densities
  - Performance is mainly controlled by
    - diffusion of Li ions
    - electron conductivity in the electrolyte
  - Recent approaches to increase performance involve
    - Use of nano-structured electrodes for shorter ion diffusion distances
    - Introduction of dopants to increase ion transport efficiency
  - However, stable performance over thousands of charge/discharge cycles has not been achieved.



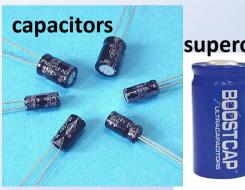


# **Expected Performance**

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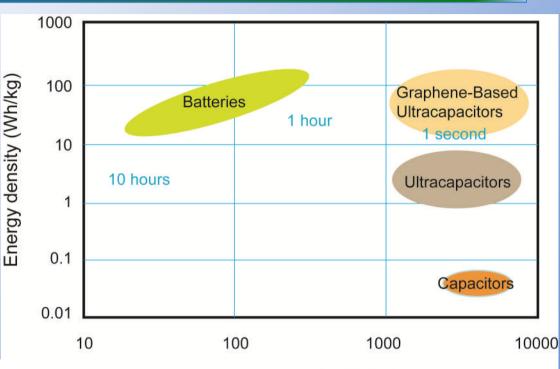
# Our graphene-based ultracapacitors:

- High power densities of ultracapacitors
- High energy densities due to huge surface area of graphene



### supercapacitors





Power density (W/kg)



Energy and power density comparison for batteries, conventional ultracapacitors, and the expected performance of graphene-based ultracapacitors. Charging times are shown in blue.



# Technical Approach

- Methods to reduce Graphene Oxide into graphene include chemical, thermal, and flash reduction
- UCLA Co-Investigator developed a light scribe lithography method that produces high quality graphene films that have high electrical conductivity and specific surface area, and can be used directly as electrodes in energy storage devices.\*
- We are producing Laser Scribed graphene as well as direct laser reduced graphene.
- Ultracapacitors are assembled with graphene sheets using liquid electrolyte



### **UCLA Laser Scribe Method**

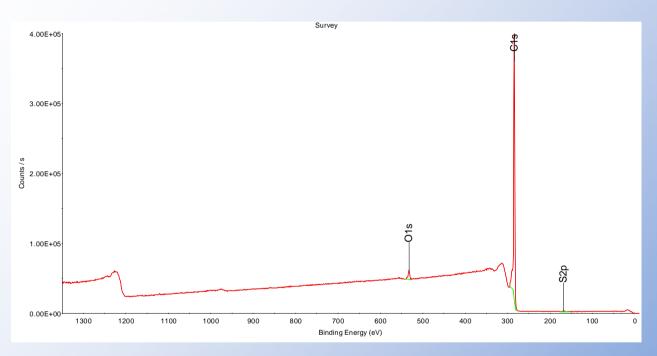


M.F. El-Kady, V.Strong, S.Dubin, R.B. Kaner, *Science* 335, 1326-1330 (2012)



# Results: XPS Analysis

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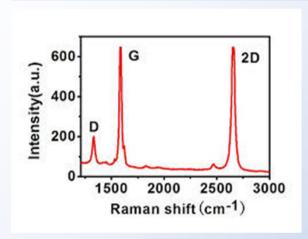


XPS survey scan of a representative graphene sample showing the relative presence of carbon (C1s peak) and oxygen (O1s peak).

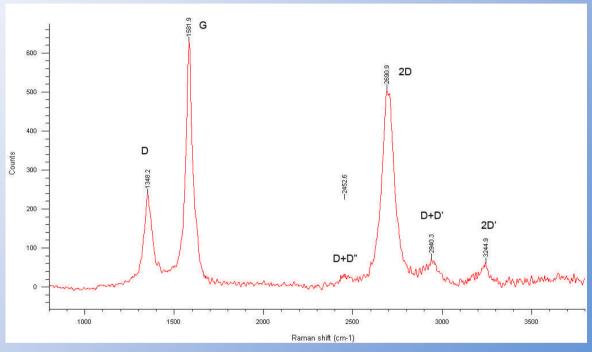
- The carbon content of the graphene sheets ranges from 96% to 98.5% while the oxygen content is in the range of 1.4% to 3%.
- In comparison, more widely used chemical reduction methods reduce oxygen content to 10% or higher. Our laser reduction method produces a more pure graphene sample.
- The carbon and oxygen content of the unreduced graphene oxide ranges between 66% to 70% and 29% to 32% respectively.



# Results: Raman Spectrum



Ideal Raman spectrum of graphene.



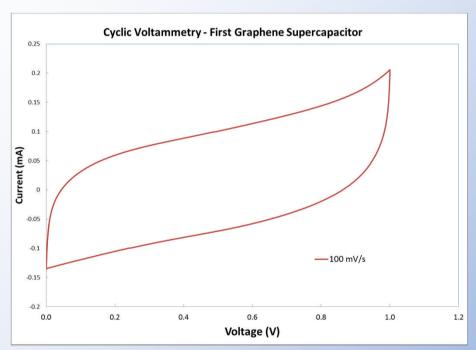
Actual Raman spectrum of a graphene sheet.

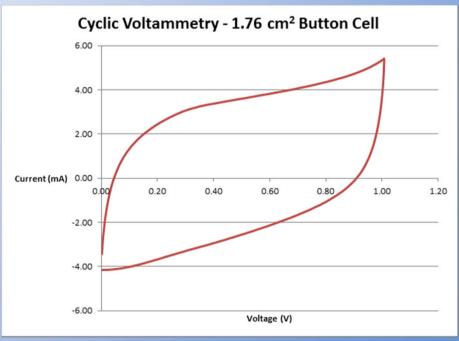
- Raman spectrum of the graphene sheet shows the G, 2D, D+D", and 2D' bands that are characteristic of graphene, as well as a Ramanforbidden band, D+D', that arises from defects.
- Defects could be edges, functional groups, or structural disorders



## Results: Ultracapacitor Performance

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Cyclic voltammetry profile for first parallel-plate graphene capacitor prototype at 100 mV/s.

Cyclic voltammetry profile for parallel-plate graphene button cell capacitor prototype at 100 mV/s.



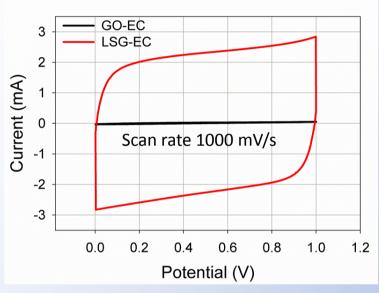
# Ultracapacitor Performance

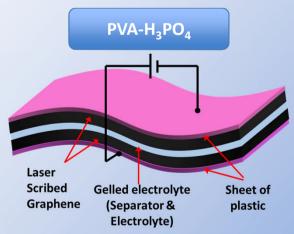
Curve	dV/dt (V/s)	Capacitance (F)	Capacitance (F/cm²)
1	1	1.38E-02	6.00E-03
2	0.1	2.45E-02	1.07E-02
3	0.01	5.50E-02	2.39E-02

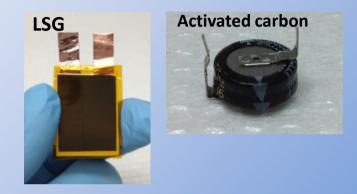
- Capacitance and capacitance per unit area values were obtained from cyclic voltammetry at different scan rates for the button cell prototype.
- Capacitance per unit area increased from 2.4 mF/cm<sup>2</sup> for the early pouch cell to 24 mF/cm<sup>2</sup>
- Results are very encouraging and show that we should be able to increase the capacitance as we scale up the devices.

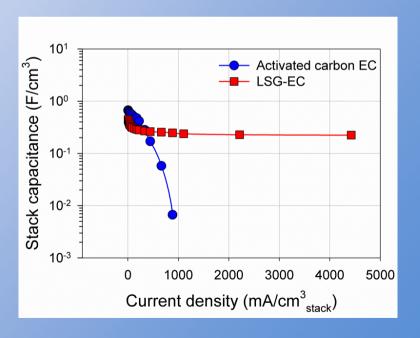


# Ultracapacitor Performance



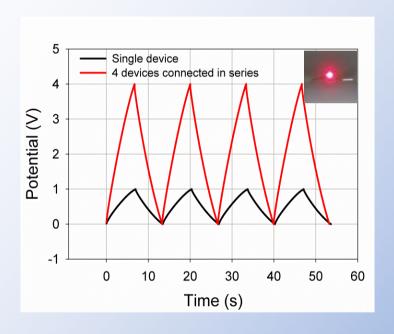




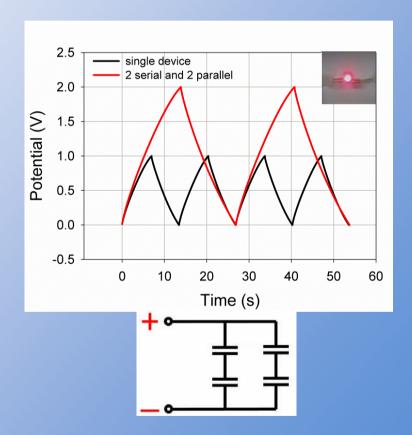




# **Tandem Supercapacitors**

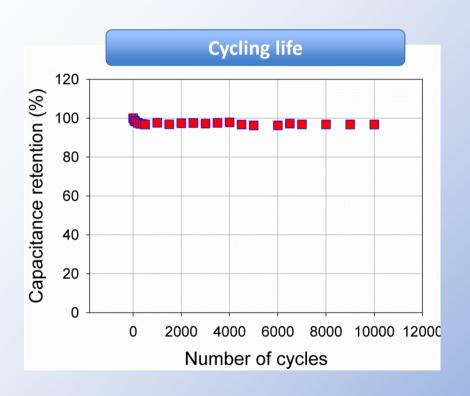








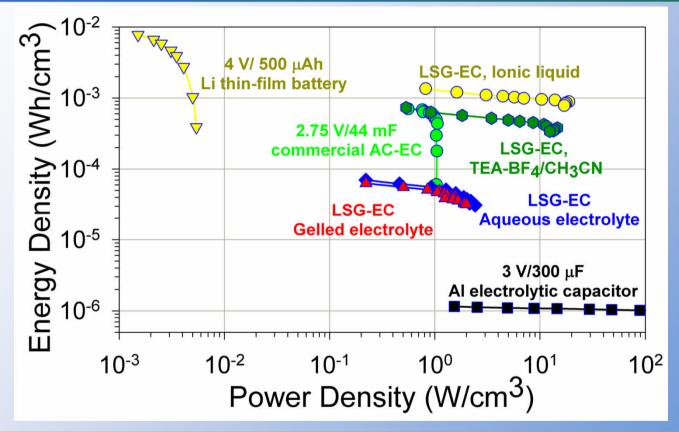
# Cycling and Shelf-Life







# LSG vs. Commercial Supercapacitors



- The plot shows the energy density and power density of the stack for all the devices tested (including current collector, active material, electrolyte and separator).
- Additional features: flexible, lightweight, current collector free and binder free

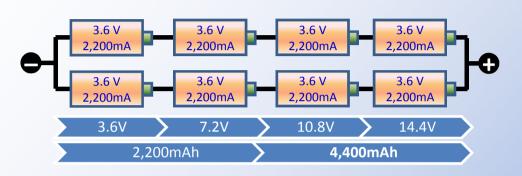


# Distribution/Dissemination

- Graphene-based unltracapacitors for aeronautics applications
  - Invited paper to be presented at the 247<sup>th</sup> ACS
     National Meeting, Dallas, TX, March 16-20, 2014



# Next Steps





- Increase in voltage produces a substantial increase in the energy density of a supercapacitor ( $E = \frac{1}{2}CV^2$ )
- Investigate new solvents and electrolytes with higher ion conductivity that would yield voltages suitable for aeronautics applications
- Investigate combinations of these electrolytes for higher performance
- Scale up graphene sheet production with our laser system
- Build prototypes to demonstrate feasibility of graphene-based ultracapacitors for aeronautics applications